

300 Area Treatability Test: In Situ Treatment of the Deep Vadose Zone and Capillary Fringe Uranium Contamination by Polyphosphate Infiltration

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Hanford 300 Area in 1962



- ▶ North & South Process Pond
Inventory 37,000 – 65,000 kg of uranium
 - 1944 – 1954: Effluents from REDOX and PUREX process development
 - 1978 – 1986: N-reactor fuels fabrication wastes
 - Enriched, natural, and depleted uranium



- ▶ Evaluate polyphosphate remediation technology for stabilization of uranium within the vadose zone and capillary fringe

Figure Source: Lindberg 2002

Conceptual Model of Uranium Remobilization During High River Stages

W ← → E

300 Area Process Trenches - Eastern Trench (Western not shown)

Backfilled in 1999

Original Trench Dimensions

Soil removal during ERA (1991) and later backfilled (1999)

Contaminated Vadose Zone

Columbia River

High River Stage

Reversed Flow during High River Stage

Normal Flow

Normal River Stage

Uranium Contamination

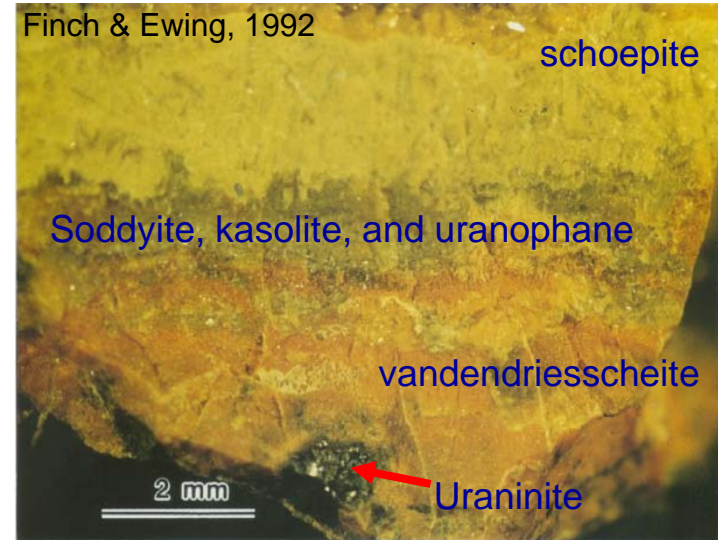
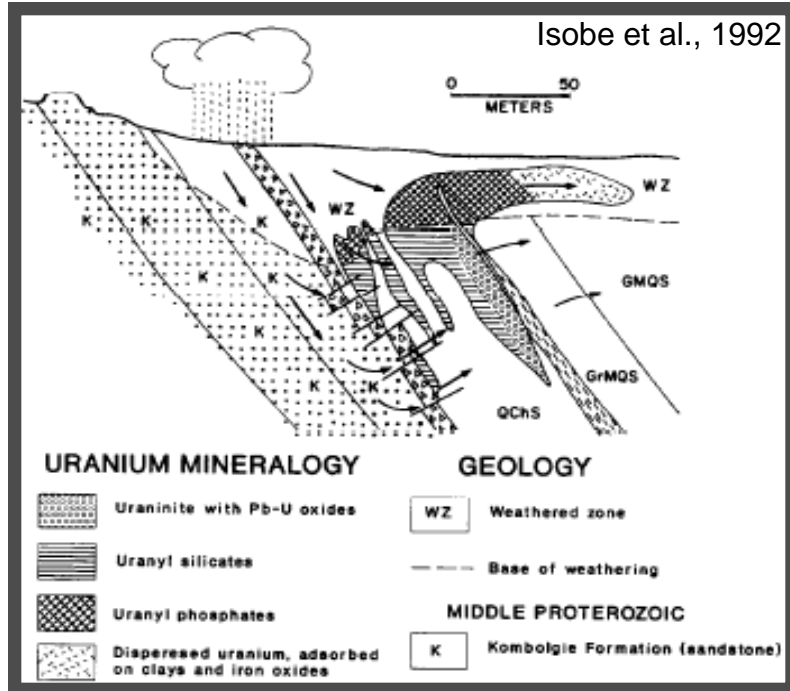
Groundwater Flow into 300 Area

Vadose Zone becomes Saturated during high river stages which remobilizes uranium contamination

Zone of leaching by higher than normal water table



Natural Attenuation of Uranium - Formation & Transformation



- ▶ Uraninite → uranyl silicates → uranyl phosphates
- ▶ Mechanisms of formation
 - Co-ppt. w/ weathering products
 - Paragenesis

- ▶ Cycling between wet and dry periods
 - Increased surface area exposed to infiltrating water
 - Separation and disintegration of layers form smaller grains
 - Expansion cracks
 - Accelerated corrosion of higher solubility uranium phases
 - Accelerated formation of secondary uranium-minerals, i.e. uranyl-phosphates

Development of Polyphosphate Technology for Treatment of the Deep Vadose Zone and Capillary Fringe Uranium Contamination

▶ Laboratory-Scale Testing

- Behavior of polyphosphate under unsaturated conditions
- Interaction & effect of polyphosphate on existing uranium mineralogy (U-rich calcite, uranophane, and meta-torbernite)
- Stability and dissolution rates of uranium minerals

▶ Predictive Simulation & Geochemical modeling

- EQ3/6 - Update the thermodynamic database to include rates of polyphosphate hydrolysis, aqueous uranium speciation, and rates of uranium mineral dissolution
- STOMP - Simulate infiltration approaches & rates
 - Evaluate the rate of uranium release and immobilization

▶ Intermediate-Scale Tests

- Infiltration Approach and Efficiency
 - Effects of heterogeneity, preferential flow paths, and mobile/immobile water
- Scaling to field test

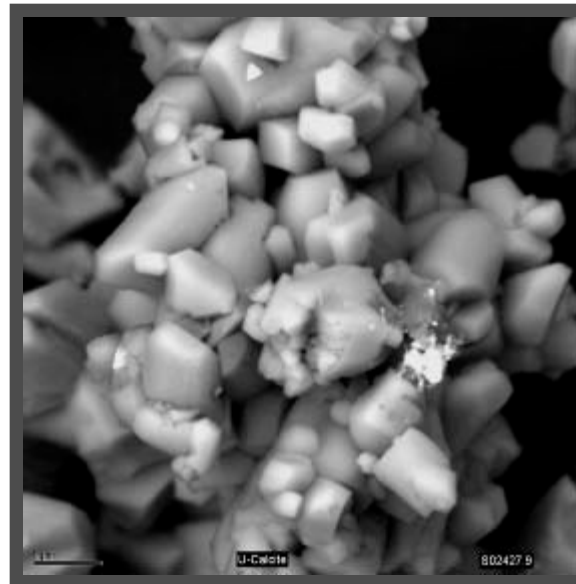
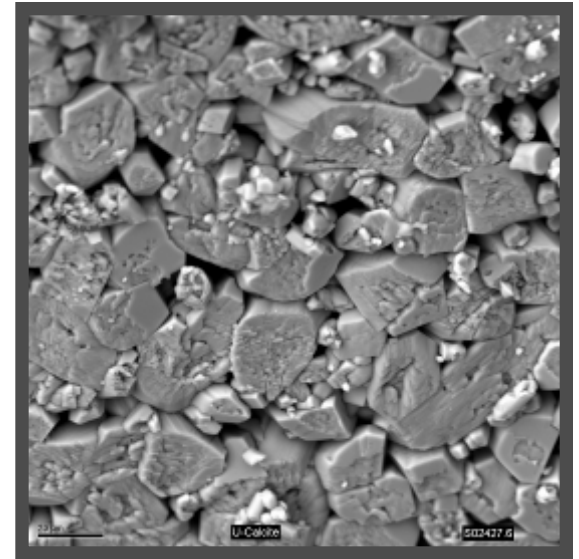
Reaction of Polyphosphate with Uranium Phases

- ▶ Changes in the chemical/mineralogical properties of the uranium phases
- ▶ Transformation of uranium phases
- ▶ Formation and identity of secondary phases



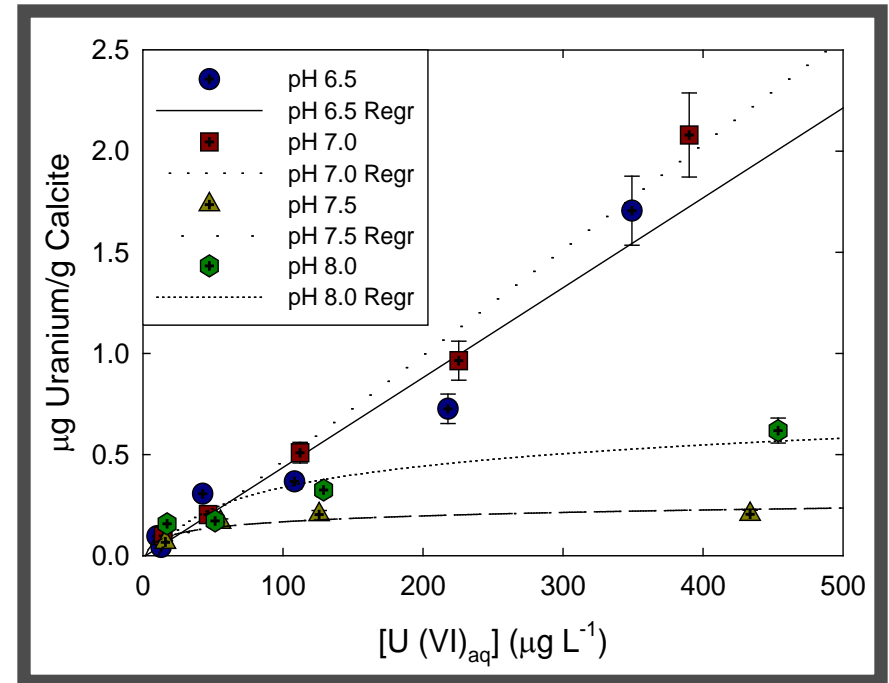
Sequestration of Uranium with Calcite

- ▶ Calcite
 - common mineral component within the Hanford subsurface
 - known sorbent for U(VI)
- ▶ Source of Ca^{2+} and CO_3^{2-} to form mobile, aqueous uranyl-carbonate species, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$, under circumneutral to alkaline conditions
- ▶ Deployment of phosphate-based remediation technologies requires understanding the interaction of uranium with calcite in the presence of aqueous phosphate.



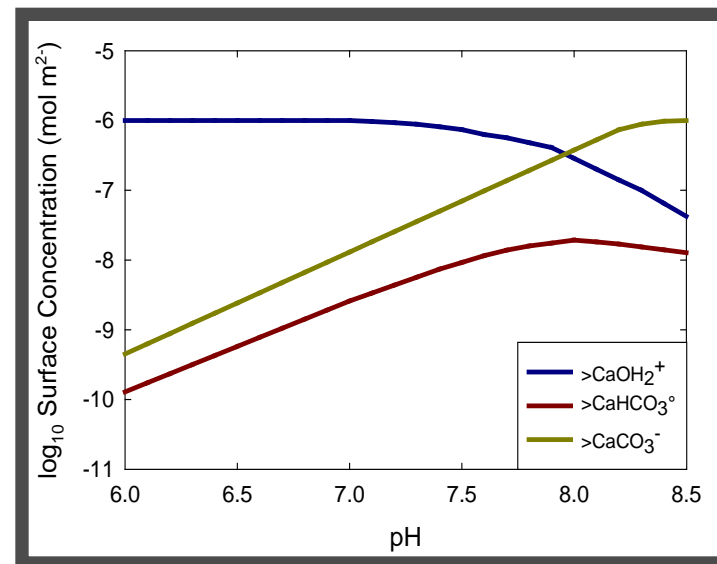
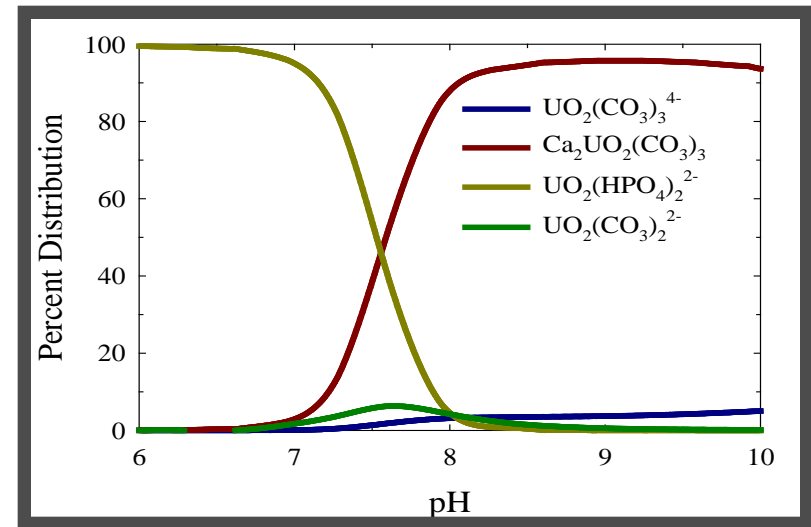
Sequestration of Uranium with Calcite

- ▶ Uptake of uranium onto calcite:
 - 0.45 μm -filtered calcite-equilibrated Hanford groundwater
 - pH range 6.5 – 8.0
 - Uranium concentration range 10 ppb to 10 ppm
 - 0.2 g calcite in 10 mL uranium-spiked solution
 - 1 week equilibration period
- ▶ Removal of uranium increased linearly over the pH range of 6.5 – 7.0.
- ▶ The concentration of uranium sequestered by calcite reaches a maximum of 0.2 – 0.6 $\mu\text{g U/g}$ calcite at pH 7.5 – 8



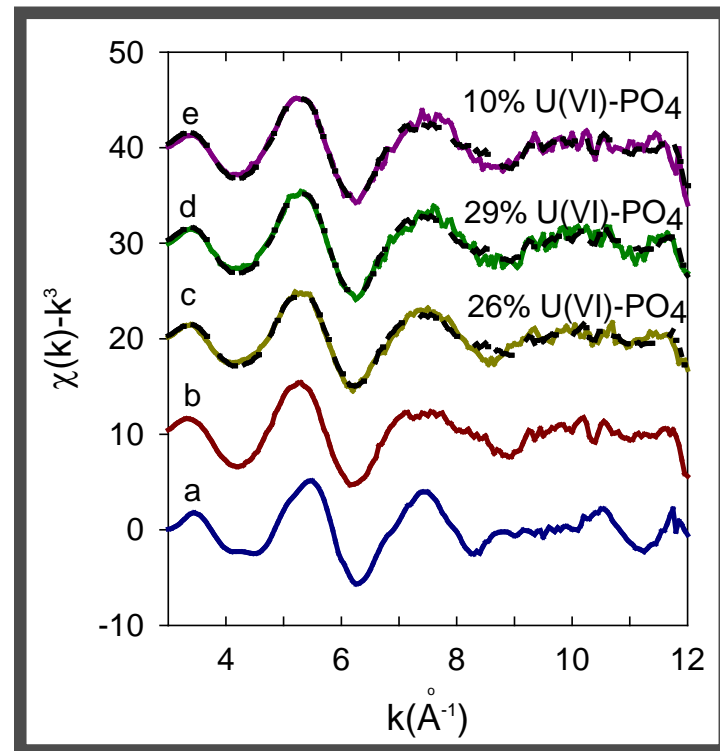
Effect of Speciation on Uranium Sequestration

- ▶ $\text{UO}_2(\text{HPO}_4)_2^{2-}$ is the dominant aqueous species predicted below pH 7.5.
- ▶ The dominant aqueous species for pH > 7.5 is the ternary species $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$.
- ▶ Dominance of cationic surface sites and anionic aqueous uranium species at pH < 7 results in greater sequestration of uranium with calcite.
- ▶ Increasing proportion of anionic surface sites and neutral aqueous species at pH values ≥ 7.5 reduces the affinity of the aqueous uranium species for the calcite surface



Transformation of U-calcite to Autunite-Group Minerals

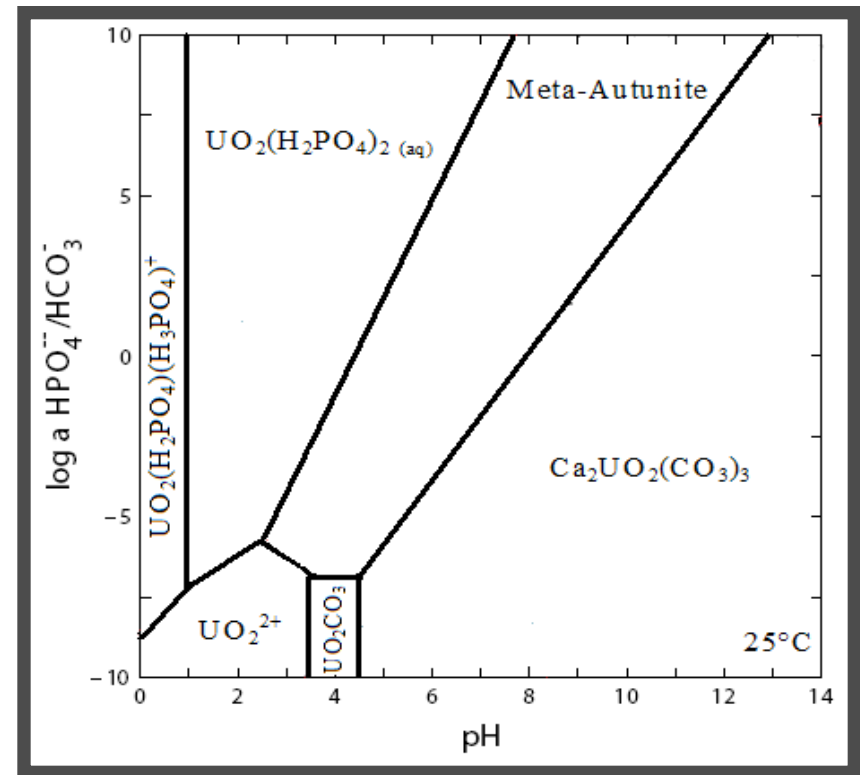
- ▶ EXAFS data show the formation of uranyl-phosphate (autunite-group) minerals on uranium-rich calcite in Hanford groundwater containing 340 ppb phosphate
- ▶ Results demonstrate the ability of autunite-group phases to form in the presence of minimal phosphate concentrations
- ▶ Suggests that the sorption of phosphorus to uranium-rich calcite may serve as an initial step in the formation of Ca-autunite



EXAFS of (a) autunite-group mineral, $X_{3-n}^{(n)+}[(\text{UO}_2)(\text{PO}_4)]_2 \cdot x\text{H}_2\text{O}$, (b) U-calcite, and calcite reacted with 60 ppm uranium in the presence of 340 ppb phosphate at (c) pH 7, (d) pH 7.5, and (e) pH 8.

Uranium Speciation and Autunite Stability

- ▶ Formation of the uranyl-phosphate phase is most prominent at pH 7.0-7.5. This is consistent with the formation of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ species at pH ≥ 7.5 and the stability of autunite
- ▶ Amount of phosphate required for meta-autunite precipitation increases as a function of pH and carbonate concentration



Polyphosphate Stabilization of U-Calcite

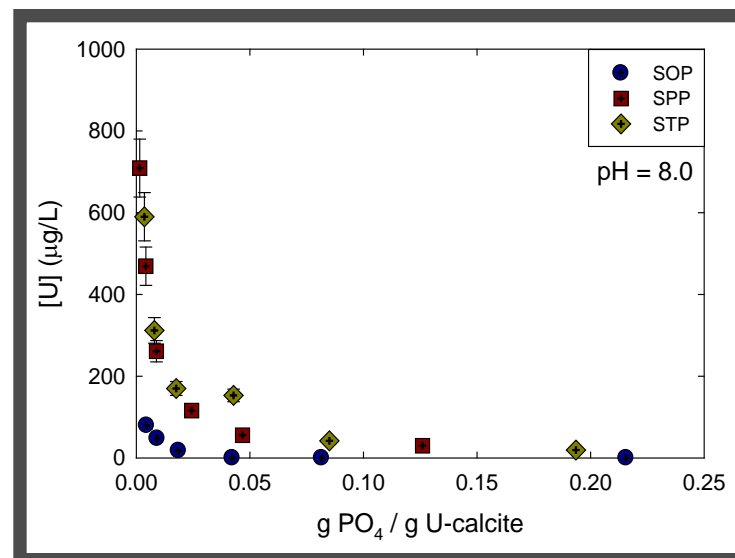
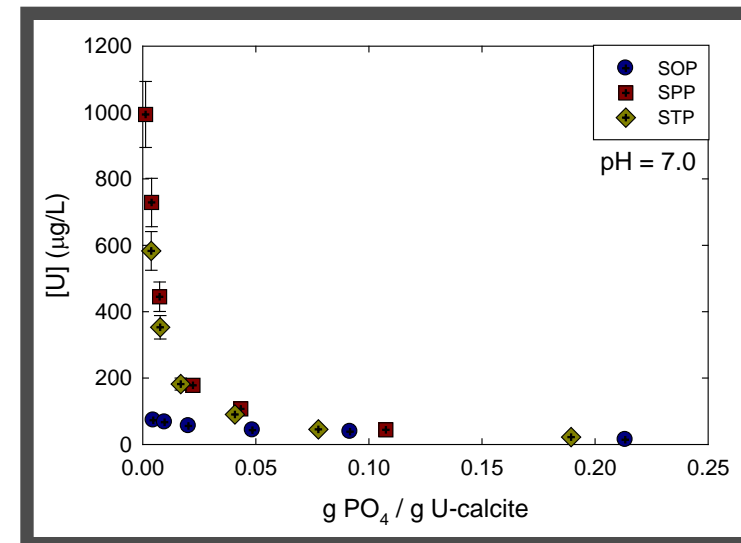
▶ Polyphosphate stabilization of U-calcite:

- 0.45 μm -filtered Hanford groundwater
- pH range 6.5 – 8.0
- 1 week equilibration period

▶ Exponential decrease in uranium over pH 6.5 – 8.0

▶ Orthophosphate provides most rapid and complete attenuation of uranium

▶ $< 30 \mu\text{g/L}$ uranium at $< 0.05 \text{ g PO}_4/\text{g U-calcite}$



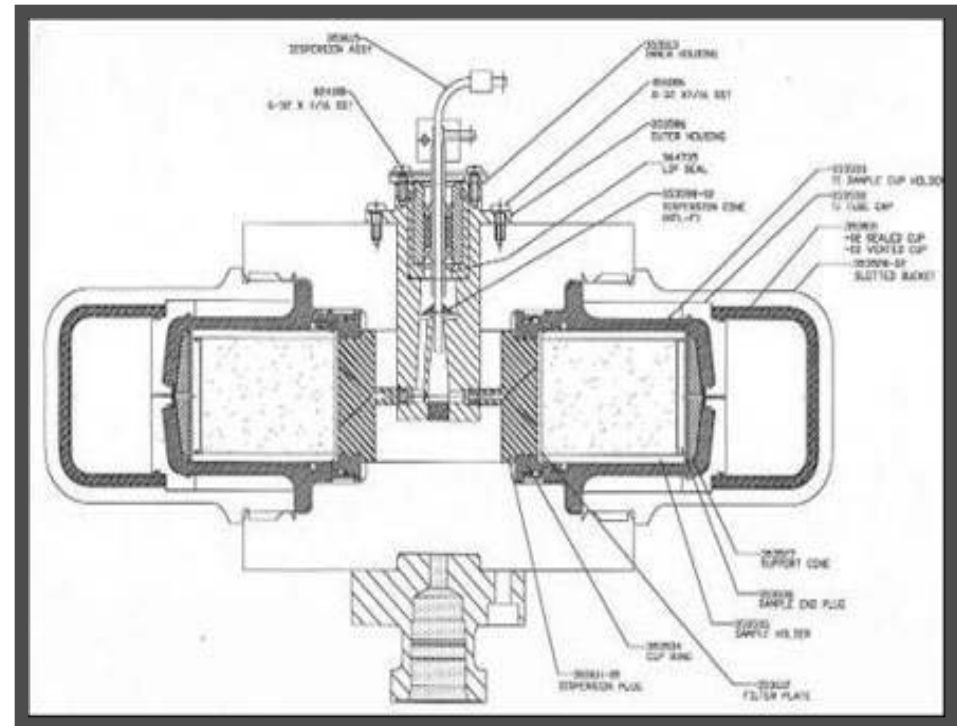
Behavior of polyphosphate under unsaturated conditions

▶ Unsaturated Flow Apparatus (UFA)

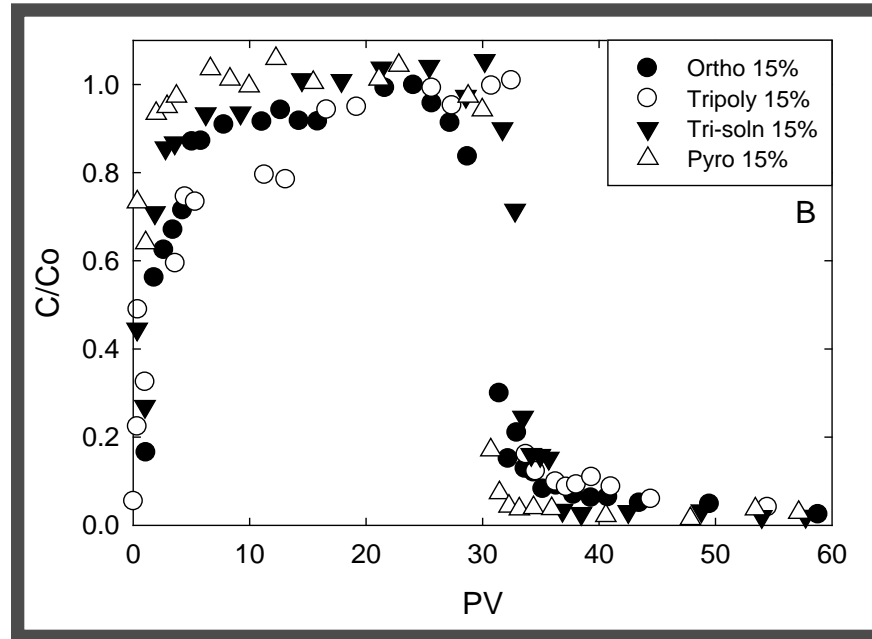
- Quantify the mobility of polyphosphate compounds as a function of water content and pore water velocity

- ▶ Lower water contents can result in decreased sorption

- Incomplete sorption due to rate limitations
- Decreased availability of sorption sites induced by two-region flow at the lower water contents
- Decrease effective pore volume



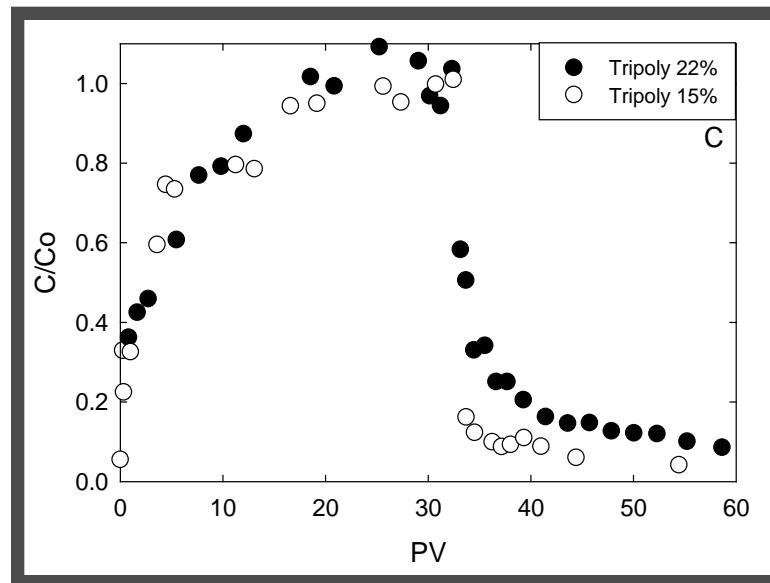
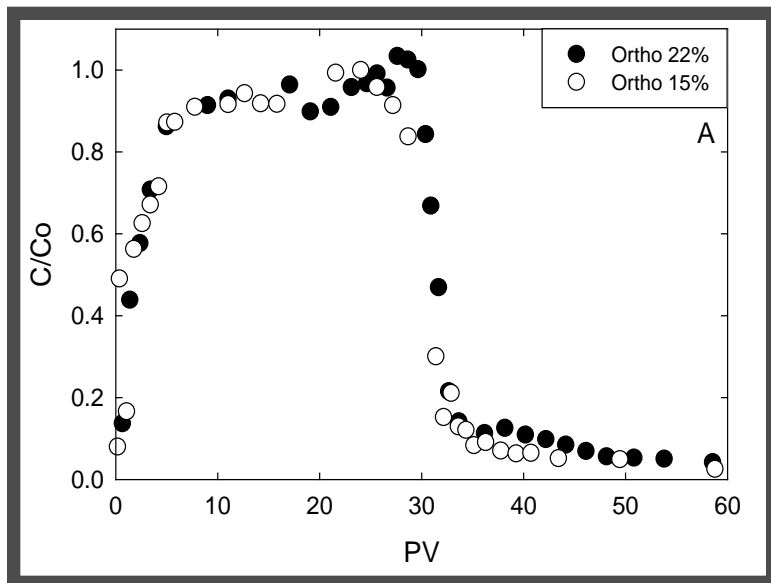
Transport of Polyphosphates



Experiment	F , $\text{cm}^3 \text{h}^{-1}$	rpm	ρ_b , g cm^{-3}	θ	V_w , mL	v , cm h^{-1}	t_0 (V_w)	% Rec.	R_{ef}	K_{d-app} , mL g^{-1}
Ortho-15-20	20.5	900	1.52	0.069	6.57	18.73	31.12	92.05	4.94	0.18
Pyro-15-20	20.7	900	1.50	0.064	6.15	20.21	30.36	98.56	2.16	0.05
Tripoly-15-20	22.7	900	1.52	0.066	6.26	21.75	33.34	96.12	5.22	0.18
Tri-soln-15-20	22.3	900	1.51	0.072	6.85	19.55	33.16	94.27	4.41	0.16

(a) F = flow rate; ρ_b = bulk density; θ = average volumetric water content (standard deviation); V_w = average pore volume; v = average pore water velocity; t_0 = step input; R_{ef} = effective retardation factor; K_{d-app} = apparent sediment water distribution coefficient based on R_{ef} .

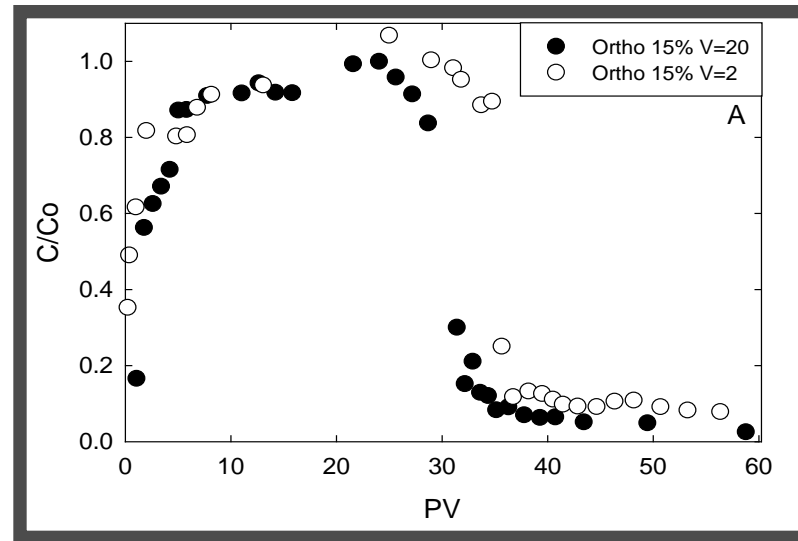
Effect of Water Content



Experiment	F , $\text{cm}^3 \text{h}^{-1}$	rpm	ρ_b , g cm^{-3}	θ	V_w , mL	v , cm h^{-1}	t_o (V_w)	% Rec.	R_{ef}	K_{d-app} , mL g^{-1}
Ortho-22-20	30.4	900	1.52	0.105	10.07	18.12	30.19	98.17	5.23	0.29
Ortho-15-20	20.5	900	1.52	0.069	6.57	18.73	31.12	92.05	4.94	0.18
Pyro-22-20	31.4	900	1.50	0.100	9.56	19.70	31.61	93.21	8.64	0.51
Pyro-15-20	20.7	900	1.50	0.064	6.15	20.21	30.36	98.56	2.16	0.05
Tripoly-22-20	32.3	900	1.52	0.098	9.37	20.68	32.93	101.94	8.44	0.48
Tripoly-15-20	22.7	900	1.52	0.066	6.26	21.75	33.34	96.12	5.22	0.18
Tri-soln-22-20	33.8	900	1.51	0.110	10.46	19.39	31.40	94.33	7.56	0.48
Tri-soln-15-20	22.3	900	1.51	0.072	6.85	19.55	33.16	94.27	4.41	0.16

(a) F = flow rate; ρ_b = bulk density; θ = average volumetric water content (standard deviation); V_w = average pore volume; v = average pore water velocity; t_o = step input; R_{ef} = effective retardation factor; K_{d-app} = apparent sediment water distribution coefficient based on R_{ef} .

Effect of Pore Water Velocity

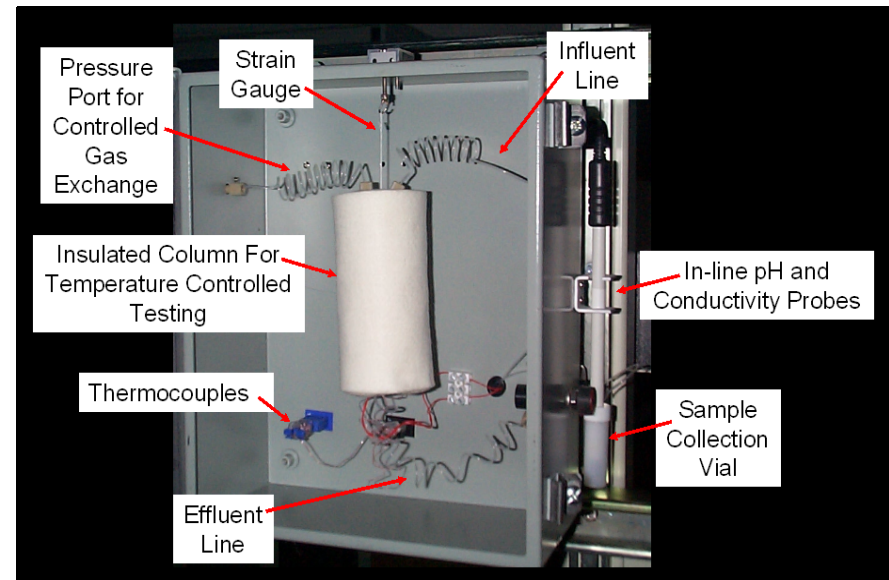


Experiment	F , $\text{cm}^3 \text{h}^{-1}$	rpm	ρ_b , g cm^{-3}	θ	V_w , mL	v , cm h^{-1}	t_o (V_w)	% Rec.	R_{ef}	K_{d-app} , mL g^{-1}
Ortho-15-20	20.5	900	1.52	0.069	6.57	18.73	31.12	92.05	4.94	0.18
Ortho-15-2	1.8	3000	1.52	0.055	5.21	2.07	37.51	97.65	4.95	0.14

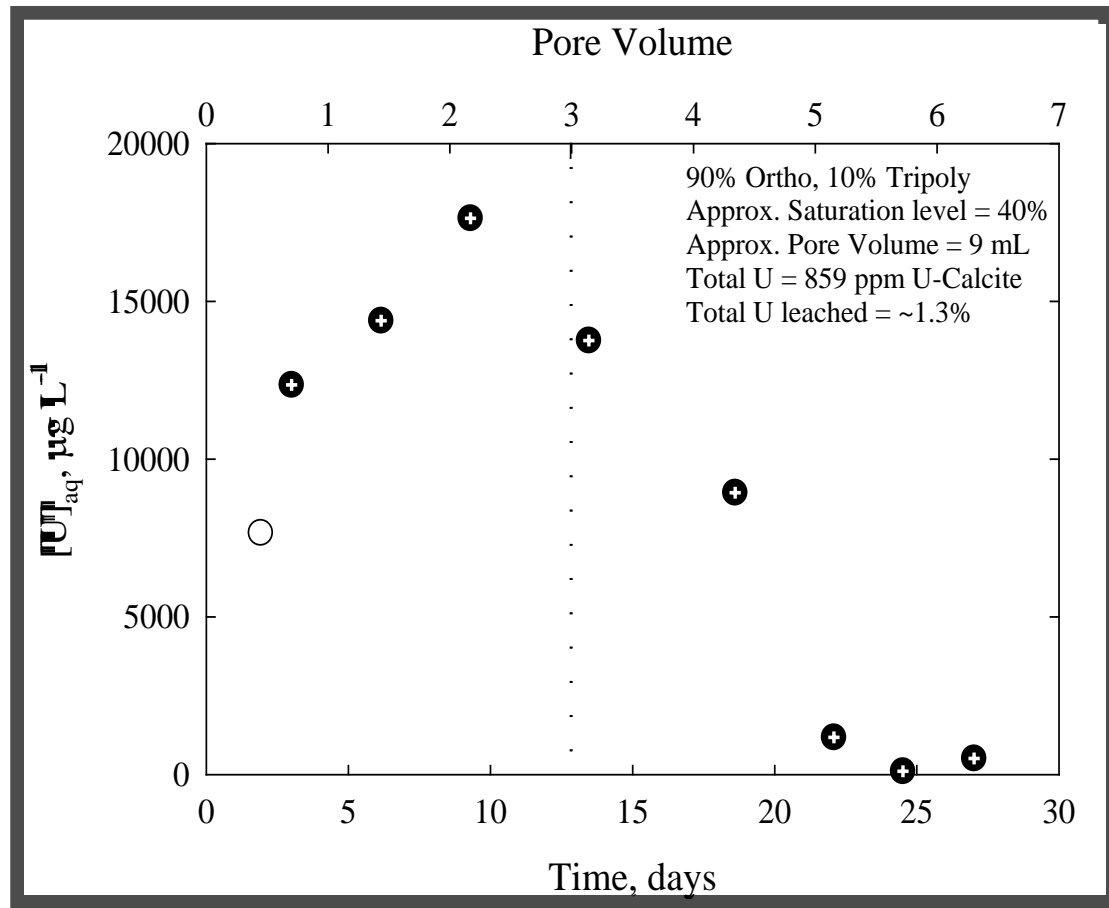
(a) F = flow rate; ρ_b = bulk density; θ = average volumetric water content (standard deviation); V_w = average pore volume; v = average pore water velocity; t_o = step input; R_{ef} = effective retardation factor; K_{d-app} = apparent sediment water distribution coefficient based on R_{ef} .

Rate and extent of polyphosphate reaction with uranium phases in the vadose and smear zone

- ▶ Pressurized Unsaturated Flow (PUF) System
 - Rate of uranium release
 - Transformation of uranium phases
 - Formation and identity of secondary phases
 - Rate of uranium immobilization
 - Extent of reaction between uranium-phases with polyphosphate

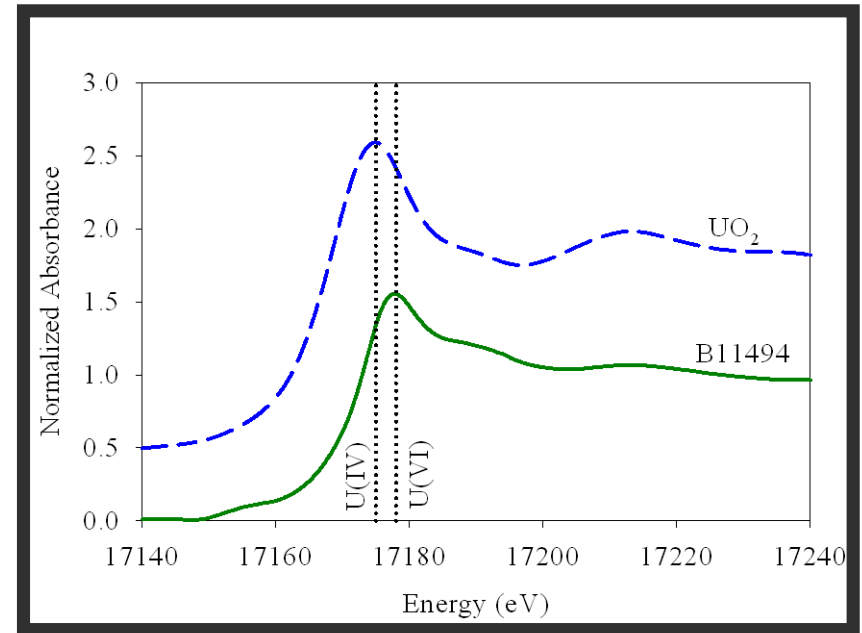


Reaction of Polyphosphate with U-rich Calcite under Unsaturated Conditions



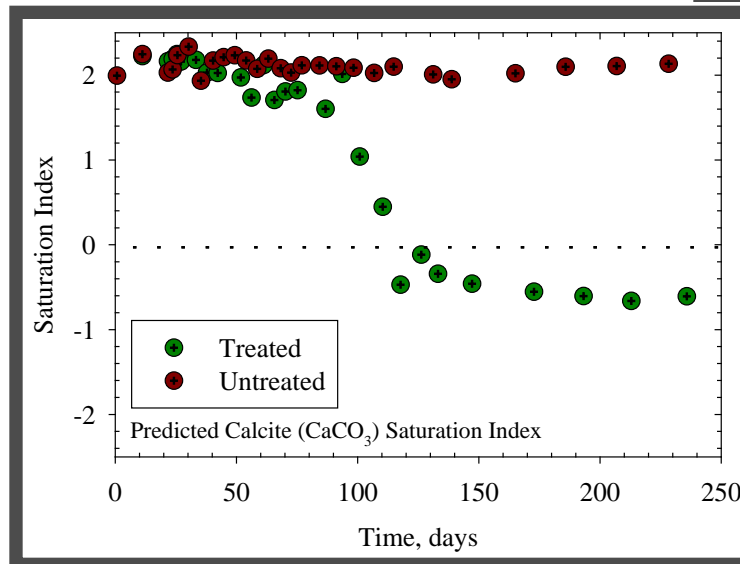
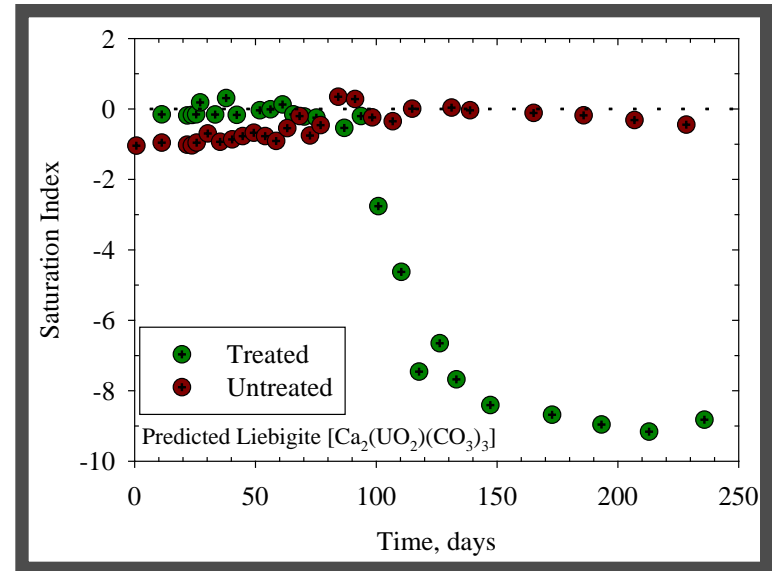
Polyphosphate Remediation of NPP Sediment under Unsaturated Conditions

- ▶ North Process Pond Sediment containing 540 ppm uranium (VI)
- ▶ Uranium in these sediments has been found to occur primarily in a form coprecipitated with calcite, CaCO_3
- ▶ Other uranium species may also be present in the sample, but only as minor components (<10%)



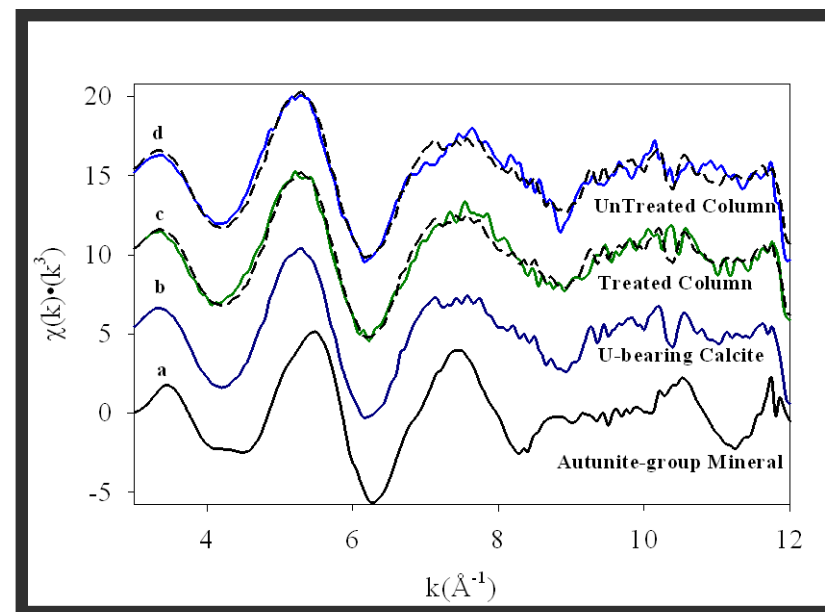
Geochemical Modeling of NPP Effluent Solution Chemistry Results

- ▶ Polyphosphate treatment decreased saturation indices for $\text{Ca-UO}_2\text{-CO}_3$ solid phases
- ▶ Subsequent release of uranium is limited by the dissolution of uranyl-phosphate rind



EXAFS Results – Polyphosphate Remediation of Uranium Contaminated 300 Area Sediments from NPP

- ▶ Transformation of ~14% of uranium to autunite-group mineral, remaining fraction co-precipitated with calcite
- ▶ Formation of an autunite group mineral “rind” on the U-calcite surface decreased flux of uranium from ~5000 $\mu\text{g L}^{-1}$ to 7 $\mu\text{g L}^{-1}$
 - < 1% total uranium leached



EXAFS of (a) autunite-group mineral, $X_{3-n}^{(n)+}[(\text{UO}_2)(\text{PO}_4)]_2 \cdot x\text{H}_2\text{O}$, (b) U-calcite, and 300 Area sediment PUF column containing ~540 mg/kg uranium as uranium co-precipitated with calcite leached with (c) 1000 ppm tripolyphosphate and (d) Hanford groundwater.

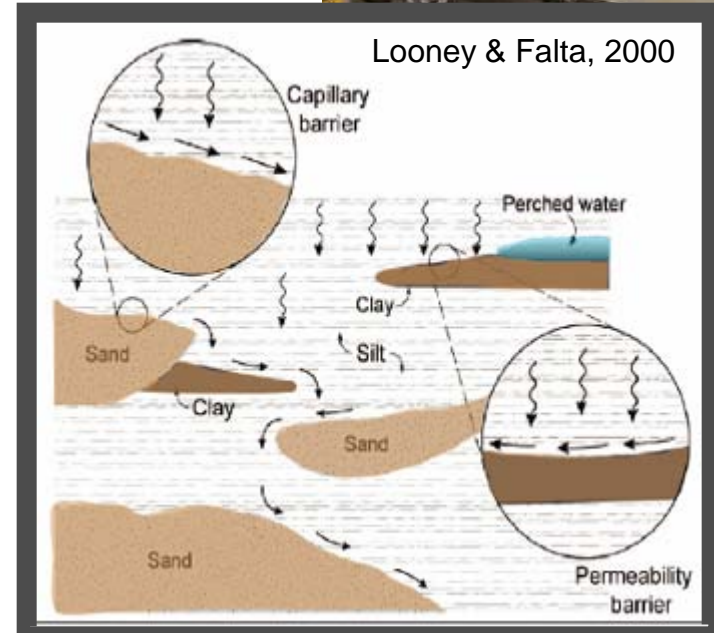
Other Results & Progress

- ▶ Quantified the transport of ortho-, pyro-, and tripolyphosphate under unsaturated conditions
- ▶ Reformulated the polyphosphate amendment for accelerated reaction rates needed for infiltration
- ▶ Quantified sequestration of uranium with calcite
- ▶ Characterized the stabilization of U-calcite by reaction with polyphosphate
- ▶ Quantified stability of relevant uranium source minerals (U-calcite, uranophane, and meta-torbernite) and rate of release of uranium as function of pH, temperature, and aqueous phosphate concentration
- ▶ Quantified the rate and extent, and characterized the interaction of ortho-, pyro-, and tripolyphosphate with relevant uranium minerals (U-calcite, uranophane, and meta-torbernite)
- ▶ Updated geochemistry within EQ3/6 & STOMP for predictive simulation of infiltration designs
- ▶ Conducting intermediate-scale tests

Intermediate Scale Tests

- Evaluate the effect of
 - variations in sediment permeability (e.g. transition from sandy-gravel to silty-sand)
 - sediment heterogeneity,
 - preferential flow paths
 - regimes of mobile/immobile water

on the infiltration emplacement and efficacy of the polyphosphate amendment for the immobilization of uranium.



Expected Outcomes

- ▶ Results from bench- and intermediate-scale testing will be used to design infiltration approach and monitoring strategy
 - Incorporate lab-scale data into a variably saturated flow and reactive transport model
 - advantages/disadvantages of surface application versus application at greater depth
- ▶ Data obtained from this study will
 - Establish the viability of the method
 - Determine how best to implement the technology in the field
 - Develop implementation cost estimates,
 - Identify implementation challenges,
 - Investigate the ability of the technology to meet remedial objectives

Earned Value Report

Polyphosphate	June	June Cum.
BCWS	\$80,000	\$850,000
BCWP	\$120,000	\$872,805
ACWP	\$112,781	\$808,901
SV	\$40,000	\$22,804
CV	\$7,219	\$63,904

- ▶ This project has no significant schedule variance.
- ▶ This project has a +8% cost variance that is associated with the addition of summer interns assisting with laboratory testing.

Fluor Funding

- ▶ 7/2/2008 - \$490,000 FY08 Funding Received from Fluor
 - Laboratory studies on uranium mineralogy and vadose zone polyphosphate transport
- ▶ Remaining EM-22 Funding, ~\$250,000, Carry over to FY09
- ▶ Field Test
 - Planning, Test Design & Construction, and Tracer Test

Acknowledgements

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- ▶ The support of the U.S Department of Energy, RL Hanford Site Groundwater Remediation Project is also gratefully acknowledged.
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- ▶ Laboratory-Scale Testing
 - Eric Pierce, Kim Griswold, Chase Bovaird, Katie Gunderson, Elsa Cordova, Emily Richards, Eric Clayton, Steven Baum, Ruby Ermi, Keith Geiszler, Mike Lindberg, Kent Parker, and Igor Kutnyakov
- ▶ Intermediate-Scale Testing
 - Mart Oostrom, Thomas Wietsma
- ▶ Predictive Simulations & Geochemical Modeling
 - Diana Bacon

Stability of Meta-Torbernite vs. Meta-Autunite

- ▶ Linear pH-dependence
 - Meta-Autunite 0.42 ± 0.08
 - Meta-Torbernite 0.52 ± 0.06
- ▶ Uranium release rates from meta-autunite and meta-torbernite minerals are within experimental error
- ▶ Uranium release from autunite ~ 6 orders of magnitude less than from UO_2 under similar conditions (Pierce et al., *J. Nuc. Mat.* 2005)

